

Title of the Invention

CATALYST BODY

Background of the Invention

5 (1) Field of the Invention

~~[0001]~~ The present invention relates to a catalyst body containing in a carrier an alkali metal and/or alkaline earth metal, particularly Li, Na, K or Ca, which is used, for example, as an NOx adsorption catalyst for purification of
10 automobile exhaust gas.

(2) Description of Related Art

~~[0002]~~ In recent years, as the regulation for automobile exhaust gas has become severer, lean burn engines and direct injection engines have come to be used widely. Thus, in
15 accordance with this change, NOx adsorption catalysts capable of effectively purifying the NOx present in an automobile exhaust gas under lean burn conditions have been put into practical use. As the NOx adsorption components used in the NOx adsorption catalysts, there are known alkali metals such
20 as K, Na, Li, Cs and the like; alkaline earth metals such as Ba, Ca and the like; rare earth elements such as La, Y and the like; and so forth. Ba, in particular, has been widely used from the start of practical application of the NOx adsorption catalysts. Lately, addition of K superior in NOx
25 adsorption ability at high temperatures has come to be tried.

~~[0003]~~ An NOx adsorption catalyst is ordinarily constituted by (a) a carrier made of an oxide type ceramic material such as cordierite, or a metal material such as Fe-Cr-Al alloy and

(b) a catalyst layer containing the above-mentioned NOx adsorption component, loaded on the carrier (a). The carrier, however, is easily corroded and deteriorated by alkali metals or some alkaline earth metals being activated under high temperature conditions derived from automobile exhaust gas, especially, Li, Na, K and Ca. In particular, there is a serious problem that a cordierite carrier made of an oxide type ceramic material generates cracks, since the carrier easily reacts with the above-mentioned alkali and alkaline earth metals, etc.

Object and Summary of the Invention

~~[0004]~~ In view of the above-mentioned conventional situations, the present invention has been made, aiming at providing a catalyst body usable, for example, as an NOx adsorption catalyst comprising a carrier and a catalyst layer containing an alkali metal and/or an alkaline earth metal, loaded on the carrier; of which carrier being prevented from the deterioration caused by the alkali metal and/or the alkaline earth metal and said body having a long period of duration.

~~[0005]~~ According to the present invention, there is provided a catalyst body comprising a carrier and a catalyst layer containing an alkali metal and/or an alkaline earth metal, loaded on the carrier, which catalyst body further contains in a carrier a substance capable of reacting with the alkali metal and/or the alkaline earth metal, dominating over the reaction between the main components of the carrier

and the alkali metal and/or the alkaline earth metal.

[0006] Incidentally, the "reaction" referred to in the present specification means not only a pure "chemical reaction" but also a phenomenon in which one substance as its function gives any influence on other substance or these two substances interact therebetween.

Detailed Description of the Invention

[0007] The catalyst body of the present invention comprises a carrier and a catalyst layer containing an alkali metal and/or an alkaline earth metal, loaded on the carrier, which catalyst further contains a substance capable of reacting with the alkali metal and/or the alkaline earth metal, dominating over the reaction between the main components of the carrier and the alkali metal and/or the alkaline earth metal, and this substance is hereinafter referred to as "anchor substance". With this catalyst body, even when the catalyst body is exposed to a high temperature during the use, the alkali metal and/or the alkaline earth metal in the catalyst layer reacts predominantly with the anchor substance; thereby its reaction with the carrier is suppressed; and resultantly, the deterioration of the carrier is suppressed.

[0008] Of the alkali metals and/or alkaline earth metals used as the catalyst component, Li, Na, K and Ca deteriorate the carrier seriously. Therefore, when such a catalyst component is used, it is preferred to use, as an anchor substance, a substance reactive predominantly with the

catalyst component. The kind of the anchor substance used differs depending upon the material of the carrier used; however, specific examples of the anchor substance are B, Al, Si, P, S, Cl, Ti, V, Cr, Mn, Ga, Ge, As, Se, Br, Zr, Mo, Sn, Sb, I and W.

~~[0009]~~ Of these anchor substances, preferred from the standpoints of non-catalyst poisoning and wide use are B, Al, Si, P, S, Ti, Cr, Mn, Br, Zr, Mo, Sn, I and W; and preferred from the standpoint of reactivity with K are Si, P, Ti, Cr, Mo and W. Si and P are most preferred from the standpoint of retention of carrier strength. P is reactive with K but deactivates noble metal components; therefore, when the catalyst layer contains a noble metal component, it is preferred that poisoning of the noble metal component by P is alleviated by appropriately selecting the form of P disposition (described later), etc. Ti, Cr, Mo and W are seldom used in purification of automobile exhaust gas, but are generally used as catalyst components and give little adverse effects on the catalytic activities of alkali metals or alkaline earth metals; therefore, they are more suitable anchor substances. These anchor substances can be used singly or in combination of a plurality of kinds.

~~[0010]~~ There is no particular restriction as to the form in which the anchor substance is added. Some anchor substances can be used as a simple substance, but a compound between anchor substance and other element is used usually. Specifically, an oxide or the like is appropriately used when the anchor substance is added as a solid (a powder); a

nitrate, a sulfate, a hydroxide, a chloride, an ammonium salt, an organic acid salt or the like is appropriately used when the anchor substance is added as a liquid (a solution). Of these compounds, preferred are such compounds as when

5 subjected to a treatment such as firing or the like, only the anchor substance and oxygen are left in the catalyst body after the treatment. For example, H_3PO_4 when the anchor substance is P and a silica sol when the anchor substance is Si are inexpensive and preferred for industrial use. A
10 compound between two or more kinds of anchor substances, such as $TiSi_2$ or the like is also preferred.

~~[0011]~~ The disposition of anchor substance in catalyst can be made in the following forms according to the following methods.

15 [Disposition of anchor substance in carrier]

~~[0012]~~ This form of disposition is preferred when the carrier is porous. This form of disposition is specifically carried out by immersing a carrier in a solution of relatively low viscosity containing at least one kind of
20 anchor substances to infiltrate the solution into the carrier to dispose the anchor substance in the carrier.

Alternatively, an anchor substance may be added to a carrier at a stage of producing the carrier. In the latter case, the anchor substance may be added as a solution, or as a solid (a
25 powder) of an oxide or the like.

[Disposition of anchor substance in catalyst layer]

~~[0013]~~ This form of disposition may be carried out by various methods, regardless of whether the carrier is porous

or not. Some of the methods are mentioned below. However, the methods usable are not restricted thereto.

(1) Method of loading a catalyst layer on a carrier and then impregnating the catalyst layer-loaded carrier with a solution containing at least one kind of anchor substances

[0014] This method has a demerit in that the anchor substance diffuses into the catalyst layer from its surface and, as a result, the anchor substance tends to be present mostly in the vicinity of the surface of the catalyst layer; meanwhile, the method has a merit in that the process of the method is simple. The anchor substance may reach as far as the interior of the catalyst layer, depending upon the thickness and density of the catalyst layer.

(2) Method of predoping at least one kind of catalyst layer components with at least one kind of anchor substances and then coating the predoped catalyst layer component on a carrier.

[0015] In this method, predoping may be conducted with the anchor substance alone or together with other catalyst layer components. Hence, this method can be classified into the following methods (a) to (e).

(a) Method of predoping a heat-resistant inorganic oxide represented by $\gamma\text{-Al}_2\text{O}_3$) with an NOx adsorption component, an anchor substance and a noble metal simultaneously, using a solution containing the three predopants

[0016] Ordinarily, in NOx adsorption catalysts, a catalyst component is loaded on a carrier in a highly dispersed state; therefore, a heat-resistant inorganic oxide having a large

specific surface area, such as $\gamma\text{-Al}_2\text{O}_3$ or the like is used as a loading component of the catalyst layer. As a catalyst component of the catalyst layer, there is used an NOx adsorption component such as alkali metal or alkaline earth metal. As other catalyst components of the catalyst layer, there is used a noble metal such as Pt, Pd or Rh so that, prior to the NOx adsorption by the above NOx adsorption component, the NO and O_2 in exhaust gas can be reacted with each other to generate NO_2 , or the NOx once occluded and then released can be reacted with the combustible components in exhaust gas and made non-harmful. In this method, a heat-resistant inorganic oxide is mixed into a solution containing an alkali metal and/or an alkaline earth metal as an NOx adsorption component, the above-mentioned noble metal and an anchor substance; the resulting mixture is subjected to firing or the like; thereby, the NOx adsorption component, the anchor substance and the noble metal are fixed on the heat-resistant inorganic oxide.

(b) Method of predoping a heat-resistant inorganic oxide represented by $\gamma\text{-Al}_2\text{O}_3$) with an NOx adsorption component, an anchor substance and a noble metal in order, using respective solutions

[0017] There is no particular restriction as to the order of predoping. With respect to the noble metal, for example, when it is used as a first predopant, the high specific surface area of the heat-resistant inorganic oxide can be utilized most effectively and, as a result, the noble metal can be dispersed in a high concentration. Meanwhile, in a

case where the noble metal is used as a last predopant, the noble metal can be fixed on the outermost surface of the heat-resistant inorganic oxide having the highest contact efficiency, and the NOx can contact with the noble metal earliest and efficiently when NOx enters into the thus-produced catalyst body. In any predoping order, it is preferable to conduct firing or the like after each predoping, for fixation of predopant(s) because a fear of redissolution in the next predoping step is made small thereby. When the NOx adsorption component, the anchor substance and the noble metal are each used by a plurality of kinds, the plurality of kinds can be used in one predoping step or in sequential predoping steps.

(c) Method which is intermediate between (a) and (b), i.e.

method of combining any two of an NOx adsorption component, an anchor substance and a noble metal (naturally, the combined two materials are used simultaneously) and conducting predoping in any order or in a predetermined order.

(d) Method of independently preparing a heat-resistant

inorganic oxide predoped with an NOx adsorption component, a heat-resistant inorganic oxide predoped with an anchor substance and a heat-resistant inorganic oxide predoped with a noble metal, and coating them on a carrier as a mixture or in respective layers.

(e) Method which is intermediate between (a) and (d), i.e. method of combining any two of an NOx adsorption component, an anchor substance and a noble metal (naturally, the combined two materials are used simultaneously) and

conducting predoping for a single heat-resistant inorganic oxide or for different heat-resistant inorganic oxides

[0018] When the NOx adsorption component, the anchor substance and the noble metal are each used by a plurality of kinds, predoping using all the kinds can be conducted in one step or predoping using each kind can be conducted for each independent heat-resistant inorganic oxide. This method can appropriately be combined with the method (c).

[0019] In any of the above methods (a) to (e), the heat-resistant inorganic oxide to be predoped is not restricted to Al_2O_3 and can also be, for example, CeO_2 , ZrO_2 , La_2O_3 which are widely used in catalysts for purification of automobile exhaust gas, compound oxides between them and compound oxides between them and Al_2O_3 . When the NOx adsorption component or the anchor substance is added into a slurry, in the form of a powder of an oxide or other compounds, it is possible, for example, to predope an NOx adsorption component oxide with an anchor substance- or noble metal-containing solution and thus conduct predoping between the NOx adsorption component, the anchor substance and the noble metal without using any heat-resistant inorganic oxide.

(3) Method of mixing a material containing at least one kind of anchor substances, directly into a slurry of an NOx adsorption components and coating the resulting mixture on a carrier

[0020] The material containing the anchor substance may be a solid or liquid (e.g. solution) of an oxide or other compound of anchor substance.

[Disposition of anchor substance-containing layer between carrier and catalyst layer]

[0021] As in the case of disposing an anchor substance in a catalyst layer, whether the carrier used is porous or not, is not critical. However, when the carrier is extremely porous, it is difficult to form, in a small thickness, an anchor substance-containing layer (an intermediate layer) between the carrier and a catalyst layer. In a specific method of forming the intermediate layer, an anchor substance-containing solution of relatively high viscosity is prepared using a sol or the like, and a carrier is immersed in the solution. Also, by applying the above-mentioned form of disposing an anchor substance in a catalyst layer, there is formed an intermediate layer containing a heat-resistant inorganic oxide or the like and an anchor substance. An intermediate layer is also formed preferably by preparing a slurry of an oxide or the like of an anchor substance and loading the slurry on a carrier. Using a sol of an anchor substance in the above slurry preparation is highly preferable because it can easily form a homogenous intermediate layer. Formation of the intermediate layer is not restricted to these methods. In any method, it is preferred to (a) conduct drying and/or firing when an intermediate layer has been formed, to fix the intermediate layer and then (b) form thereon an NO_x adsorption catalyst layer.

[0022] In any of the above disposition forms, it is preferred to conduct drying and/or firing for fixation each

time when impregnation, predoping, coating or the like has been completed. When the fixation of the catalytic layer is made by firing, the firing temperature is preferably 500 to 800°C. Allowing one or different kinds of anchor substances to be present in a catalyst by using a plurality of disposition forms, is preferred because a higher suppressability of carrier deterioration is obtained. For example, disposition of Ti in a catalyst layer, and/or formation of a Si-containing zeolite intermediate layer, and disposition of Si and/or P in a carrier is a preferred combination of disposition forms.

~~[0023]~~ In the catalyst body of the present invention, the shape of the carrier is not critical. When there is used a carrier having any shape of monolith honeycomb, pellets, beads, ring, etc., the above-mentioned suppressability of carrier deterioration is attained. The suppressability is largest when there is used a honeycomb carrier constituted by a large number of passages (cells) surrounded by thin partition walls.

~~[0024]~~ As the material for honeycomb carrier, there are preferably used, for example, ceramics such as cordierite, mullite, alumina and the like; metallic foils made of a heat-resistant stainless steel such as Fe-Cr-Al alloy or the like; and honeycomb structures shaped by powder metallurgy. When there is used a carrier made of cordierite highly reactive with Li, Na, K and Ca, the suppressability of carrier deterioration is largest.

~~[0025]~~ The shape of the passages (cells) of honeycomb

carrier can be any of circular, polygonal, corrugated, etc. The external shape of honeycomb carrier can be one compatible with the internal shape of an exhaust gas system in which the honeycomb carrier is accommodated.

5 ~~[0026]~~ The cell density of honeycomb carrier is not critical, either; however, it is preferably 6 to 1,500 cells/in.² (0.9 to 233 cells/cm²). The thickness of the partition walls of honeycomb carrier is preferably 20 to 2,000 μ m. When the partition walls have a small thickness of
10 20 to 200 μ m, the diffusion of alkali metal and/or alkaline earth metal from the catalyst layer to the center of the wall thickness of carrier is easy and the deterioration of the carrier is serious; therefore, in the case of such a small thickness of partition walls, the catalyst body of the
15 present invention is particularly effective and shows a high effect for suppression of carrier deterioration.

~~[0027]~~ The amount of the anchor substance used in the catalyst is preferably 0.05 to 10 equivalents, more preferably 0.1 to 5 equivalents relative to the alkali metal
20 and/or alkaline earth metal (e.g. Li, K, Na or Ca) which coexists with the anchor substance and reacts therewith to form a compound. The amount of the alkali metal and/or alkaline earth metal coexisting with the anchor substance should be appropriately determined based on the unit volume
25 of catalyst. When the amount of the anchor substance is less than 0.05 equivalent, there is no effect for suppression of carrier deterioration; when the amount is more than 10 equivalents, the effect is flat and shows no further increase.

When the amount is less than 0.1 equivalent, the effect for suppression of carrier deterioration is small; when the amount is more than 5 equivalents, the cost incurred is high for the effect obtained. The absolute amount of the anchor substance is preferably 0.5 to 100 g (in terms of anchor substance element) per liter of catalyst unit volume. When the absolute amount of the anchor substance is less than 0.5 g per liter, only a small effect for suppression of carrier deterioration is obtained. When the anchor substance is loaded in an amount exceeding 100 g per liter on one carrier together with an NOx adsorption catalyst layer and when the carrier is a honeycomb carrier, there is a fear of cell plugging. From the overall standpoint of the effect for suppression of carrier deterioration, the incurred cost, the loadability, etc., the amount of the anchor substance is preferably 2 to 60 g, more preferably 10 to 50 g per liter of catalyst unit volume.

[0028] The catalyst body of the present invention can be used simultaneously with other purifiers used in an exhaust gas system, such as NOx adsorption catalyst made of a different component, other catalyst typified by a three-way catalyst, co-catalyst, HC adsorbent and the like. In that case, the other purifiers may be mixed with the catalyst layer of the present catalyst or may be superimposed on the present catalyst in layers. Or, the present catalyst may be used in appropriate combination with these other purifiers in an exhaust gas system.

Examples

[0029] The present invention is described in more detail below by way of Examples. However, the present invention is in no way restricted to these Examples.

5 [Production of slurries for wash-coating of NOx adsorption catalyst]

(K catalyst slurry)

[0030] A commercially available γ -Al₂O₃ powder having a specific surface area of 200 m²/g was immersed in a solution
10 obtained by mixing an aqueous (NH₃)Pt(NO₂)₂ solution and an aqueous KNO₃ solution. The resulting material was stirred for 2 hours in a pot mill. The material after stirring was subjected to vaporization to dryness to remove the water. The resulting solid was subjected to dry disintegration,
15 followed by firing in an electric furnace at 600°C for 3 hours, to obtain a (Pt + K)-predoped γ -Al₂O₃ powder. To the powder were added an Al₂O₃ sol and water. The resulting mixture was subjected to wet grinding in a pot mill to prepare a slurry for wash-coating. The relative quantities
20 of γ -Al₂O₃, Pt and K were adjusted at the above mixing and immersion stage so that when the above slurry was wash-coated on a honeycomb carrier and the slurry-coated honeycomb carrier was fired and, in the resulting catalyst, the amount of K catalyst loaded was 100 g per liter of honeycomb, the
25 amount of Pt element became 30 g per cft of honeycomb (1.06 g per liter) and the amount of K element became 20 g per liter of honeycomb. The Al₂O₃ sol was added in such an amount that its solid content expressed as Al₂O₃ became 5% by weight of

the total Al_2O_3 ; and the water was added so that the resulting slurry had an appropriate viscosity allowing easy wash-coating.

(Na catalyst slurry)

- 5 ~~[0031]~~ An Na catalyst slurry was prepared in the same manner as for the K catalyst slurry except that an aqueous NaNO_3 solution was used in place of the aqueous KNO_3 solution and the amount of Na was set at 11.8 g per liter.

(Li catalyst slurry)

- 10 [0032] A Li catalyst slurry was prepared in the same manner as for the K catalyst slurry except that an aqueous LiNO_3 solution was used in place of the aqueous KNO_3 solution and the amount of Li was set at 3.6 g per liter.

[Production of NOx adsorption catalysts]

- 15 (Example 1)

- ~~[0033]~~ First, a cordierite honeycomb carrier [partition wall thickness = 6 mil (0.15 mm), cell density = 400 cpsi (62 cells/cm²), porosity = 30%] was immersed in an aqueous H_3PO_4 solution. Since the carrier was porous, the aqueous H_3PO_4 solution infiltrated into the interior of each cell wall. The excessive solution in the cells was removed by blowing, after which the carrier was dried. The amount of H_3PO_4 loaded was adjusted so that the moles of P element per unit volume of honeycomb carrier became 0.67 time the moles of the K element contained in the K catalyst later wash-coated and loaded. When one time of immersion and drying failed to give a desired H_3PO_4 amount, the step of immersion and drying was repeated until the amount was reached. The honeycomb after
- 20
- 25

drying was fired in an electric furnace at 700°C for 1 hour.

On this honeycomb after firing was wash-coated the above-mentioned K catalyst slurry (hereinafter, "the above-mentioned K catalyst slurry" refers to the initial slurry

5 before adjustment of the relative quantities of γ - Al_2O_3 , Pt and K, mentioned in the above production of K catalyst slurry, and the coated honeycomb was dried. This wash-coating and drying step was repeated if necessary until the amount of K catalyst loaded became 100 g per liter. The resulting
10 honeycomb was fired in an electric furnace at 600°C for 1 hour, whereby an NOx adsorption catalyst 1 was obtained.

(Example 2)

~~[0034]~~ An NOx adsorption catalyst 2 was obtained in the same manner as in Example 1 except that (1) an aqueous
15 $(\text{NH}_4)_2[\text{TiO}(\text{C}_2\text{O}_4)_2]$ solution was used in place of the aqueous H_3PO_4 solution, (2) the amount of $(\text{NH}_4)_2[\text{TiO}(\text{C}_2\text{O}_4)_2]$ loaded was adjusted so that the moles of Ti element per unit volume of honeycomb carrier became 0.1 time the moles of the K element contained in the K catalyst later wash-coated and loaded, and
20 (3) the cordierite honeycomb carrier was immersed in the aqueous $(\text{NH}_4)_2[\text{TiO}(\text{C}_2\text{O}_4)_2]$ solution and dried, and the dried honeycomb was fired at 700°C for 1 hour.

(Example 3)

~~[0035]~~ A slurry obtained by mixing a TiO_2 sol and a TiO_2
25 powder was wash-coated on the same cordierite honeycomb carrier as used in Example 1, and the coated cordierite honeycomb carrier was dried. The amount of TiO_2 loaded was adjusted so that the moles of total Ti element (from the TiO_2

sol and the TiO_2 powder) per unit volume of honeycomb carrier became equal to the moles of the K element contained in the K catalyst later wash-coated and loaded. When one time of wash-coating and drying failed to give a desired TiO_2 amount, the step of wash-coating and drying was repeated until the amount was reached. The honeycomb after drying was fired in an electric furnace at 700°C for 1 hour to form a TiO_2 intermediate layer. On this honeycomb after firing was wash-coated the above-mentioned K catalyst slurry, and the resulting honeycomb was dried. This wash-coating and drying step was repeated if necessary until the amount of K catalyst loaded became 100 g per liter. The resulting honeycomb was fired in an electric furnace at 600°C for 1 hour, whereby an NO_x adsorption catalyst 3 was obtained.

(Example 4)

~~[0036]~~ An NO_x adsorption catalyst 4 was obtained in the same manner as in Example 3 except that the above-mentioned Na catalyst slurry was used in place of the K catalyst slurry.

(Example 5)

~~[0037]~~ An NO_x adsorption catalyst 5 was obtained in the same manner as in Example 3 except that the above-mentioned Li catalyst slurry was used in place of the K catalyst slurry.

(Example 6)

~~[0038]~~ A K catalyst slurry was produced in the same manner as in the above-mentioned production of K catalyst slurry except that a TiO_2 sol was used in place of the Al_2O_3 sol. The amount of TiO_2 sol used was adjusted so that, in later wash-coating, the moles of Ti element per unit volume of

honeycomb carrier became equal to the moles of K element. The slurry produced was wash-coated on the same cordierite honeycomb carrier as used in Example 1, and dried. This wash-coating and drying step was repeated if necessary until the amount of K catalyst loaded became 100 g per liter. Then, the resulting honeycomb was fired in an electric furnace at 600°C for 1 hour to obtain an NOx adsorption catalyst 6.

(Example 7)

[0039] In mixing an aqueous $(\text{NH}_3)\text{Pt}(\text{NO}_2)_2$ solution and an aqueous KNO_3 solution in the above-mentioned production of K catalyst slurry, an aqueous $(\text{NH}_4)_2[\text{TiO}(\text{C}_2\text{O}_4)_2]$ solution was also mixed to obtain a K catalyst slurry containing a (Pt + K + Ti)-predoped $\gamma\text{-Al}_2\text{O}_3$ powder. In this case, the relative quantities of $\gamma\text{-Al}_2\text{O}_3$, Pt, K and Ti were adjusted at the above mixing and immersion stage so that when the above slurry was wash-coated on a honeycomb carrier and the slurry-coated honeycomb carrier was fired and, in the resulting catalyst, the amount of K catalyst loaded was 100 g per liter of honeycomb, the amount of Pt element became 30 g per cft of honeycomb (1.06 g per liter), the amount of K element became 20 g per liter of honeycomb, and the moles of Ti element became equal to the moles of K element. The slurry was wash-coated on the same cordierite honeycomb carrier as used in Example 1, and dried. This wash-coating and drying step was repeated if necessary until the amount of K catalyst loaded became 100 g per liter. The resulting honeycomb was fired in an electric furnace at 600°C for 1 hour, whereby an NOx adsorption catalyst 7 was obtained.

(Example 8)

[0040] A TiO_2 powder was added to the K catalyst slurry obtained in the above-mentioned production of K catalyst slurry, in such an amount that the moles of Ti element per unit volume of honeycomb carrier became equal to the moles of K element. The TiO_2 powder-added slurry was wash-coated on the same cordierite honeycomb carrier as used in Example 1, and dried. This wash-coating and drying step was repeated if necessary until the amount of K catalyst loaded became 100 g per liter. The resulting honeycomb was fired in an electric furnace at 600°C for 1 hour, whereby an NO_x adsorption catalyst 8 was obtained.

(Example 9)

[0041] An NO_x adsorption catalyst 9 was obtained in the same manner as in Example 8 except that the TiO_2 powder was added in such an amount that the moles of Ti element per unit volume of honeycomb carrier became 0.1 time the moles of K element.

(Example 10)

[0042] An NO_x adsorption catalyst 10 was obtained in the same manner as in Example 2 except that (1) an aqueous $\text{Cr}(\text{NO}_3)_3$ solution was used in place of the aqueous $(\text{NH}_4)_2[\text{TiO}(\text{C}_2\text{O}_4)_2]$ solution and (2) the amount of $\text{Cr}(\text{NO}_3)_3$ loaded was adjusted so that the moles of Cr element per unit volume of honeycomb carrier became 0.1 time the moles of the K element contained in the K catalyst later wash-coated and loaded.

(Example 11)

[0043] An NOx adsorption catalyst 11 was obtained in the same manner as in Example 3 except that the cordierite honeycomb carrier was changed to a metal honeycomb carrier (made of a Fe-Cr-Al type metal foil, partition wall thickness = 2 mil (0.05 mm), cell density = 370 cpsi (57.5 cells/cm²)).
5 (Example 12)

[0044] An NOx adsorption catalyst 12 was obtained in the same manner as in Example 1 except that the amount of H₃PO₄ loaded was adjusted so that the moles of P element per unit
10 volume of honeycomb carrier became 2.21 times the moles of the K element contained in the K catalyst later wash-coated and loaded.
(Example 13)

[0045] An NOx adsorption catalyst 13 was obtained in the same manner as in Example 1 except that the amount of H₃PO₄ loaded was adjusted so that the moles of P element per unit
15 volume of honeycomb carrier became 1.52 times the moles of the K element contained in the K catalyst later wash-coated and loaded.
(Example 14)

[0046] An NOx adsorption catalyst 14 was obtained in the same manner as in Example 1 except that the amount of H₃PO₄ loaded was adjusted so that the moles of P element per unit
20 volume of honeycomb carrier became 1.24 times the moles of the K element contained in the K catalyst later wash-coated and loaded.
(Example 15)

[0047] An NOx adsorption catalyst 15 was obtained in the

same manner as in Example 1 except that the amount of H_3PO_4 loaded was adjusted so that the moles of P element per unit volume of honeycomb carrier became 0.14 time the moles of the K element contained in the K catalyst later wash-coated and loaded.

(Example 16)

[0048] An NOx adsorption catalyst 16 was obtained in the same manner as in Example 1 except that the amount of H_3PO_4 loaded was adjusted so that the moles of P element per unit volume of honeycomb carrier became 0.028 time the moles of the K element contained in the K catalyst later wash-coated and loaded.

(Example 17)

[0049] An NOx adsorption catalyst 17 was obtained in the same manner as in Example 1 except that (1) a silica sol was used in place of the aqueous H_3PO_4 solution and (2) the amount of silica sol loaded was adjusted so that the moles of Si element per unit volume of honeycomb carrier became 2.16 times the moles of the K element contained in the K catalyst later wash-coated and loaded.

(Example 18)

[0050] An NOx adsorption catalyst 18 was obtained in the same manner as in Example 17 except that the amount of silica sol loaded was adjusted so that the moles of Si element per unit volume of honeycomb carrier became 1.79 times the moles of the K element contained in the K catalyst later wash-coated and loaded.

(Example 19)

[0051] An NOx adsorption catalyst 19 was obtained in the same manner as in Example 17 except that the amount of silica sol loaded was adjusted so that the moles of Si element per unit volume of honeycomb carrier became 1.46 times the moles of the K element contained in the K catalyst later wash-coated and loaded.

(Example 20)

[0052] An NOx adsorption catalyst 20 was obtained in the same manner as in Example 17 except that the amount of silica sol loaded was adjusted so that the moles of Si element per unit volume of honeycomb carrier became 0.79 time the moles of the K element contained in the K catalyst later wash-coated and loaded.

(Example 21)

[0053] An NOx adsorption catalyst 21 was obtained in the same manner as in Example 17 except that the amount of silica sol loaded was adjusted so that the moles of Si element per unit volume of honeycomb carrier became 0.16 time the moles of the K element contained in the K catalyst later wash-coated and loaded.

(Example 22)

[0054] An NOx adsorption catalyst 22 was obtained in the same manner as in Example 17 except that the amount of silica sol loaded was adjusted so that the moles of Si element per unit volume of honeycomb carrier became 0.033 time the moles of the K element contained in the K catalyst later wash-coated and loaded.

(Example 23)

[0055] An NOx adsorption catalyst 23 was obtained in the same manner as in Example 2 except that the amount of $(\text{NH}_4)_2[\text{TiO}(\text{C}_2\text{O}_4)_2]$ loaded was adjusted so that the moles of Ti element per unit volume of honeycomb carrier became equal to the moles of the K element contained in the K catalyst later wash-coated and loaded.

(Example 24)

[0056] An NOx adsorption catalyst 24 was obtained in the same manner as in Example 10 except that the amount of $\text{Cr}(\text{NO}_3)_3$ loaded was adjusted so that the moles of Cr element per unit volume of honeycomb carrier became equal to the moles of the K element contained in the K catalyst later wash-coated and loaded.

(Example 25)

[0057] In mixing an aqueous $(\text{NH}_3)\text{Pt}(\text{NO}_2)_2$ solution and an aqueous KNO_3 solution in the above-mentioned production of K catalyst slurry, an aqueous H_3PO_4 solution was also mixed to obtain a K catalyst slurry containing a (Pt + K + P)-predoped $\gamma\text{-Al}_2\text{O}_3$ powder. In this case, the relative quantities of $\gamma\text{-Al}_2\text{O}_3$, Pt, K and P were adjusted at the above mixing and immersion stage so that when the above slurry was wash-coated on a honeycomb carrier and the slurry-coated honeycomb carrier was fired and, in the resulting catalyst, the amount of K catalyst loaded was 100 g per liter of honeycomb, the amount of Pt element became 30 g per cft of honeycomb (1.06 g per liter), the amount of K element became 20 g per liter of honeycomb, and the moles of P element became 1.24 times the moles of K element. The slurry was wash-coated on the same

cordierite honeycomb carrier as used in Example 1, and dried. This wash-coating and drying step was repeated if necessary until the amount of K catalyst loaded became 100 g per liter. The resulting honeycomb was fired in an electric furnace at
5 600°C for 1 hour, whereby an NOx adsorption catalyst 25 was obtained.

(Example 26)

[0058] A K catalyst slurry was produced in the same manner as in the above-mentioned production of K catalyst slurry
10 except that a SiO₂ sol was used in place of the Al₂O₃ sol. The amount of SiO₂ sol used was adjusted so that, in later wash-coating and loading, the moles of Si element per unit volume of honeycomb carrier became 1.46 times the moles of K element. The slurry produced was wash-coated on the same
15 cordierite honeycomb carrier as used in Example 1, and dried. This wash-coating and drying step was repeated if necessary until the amount of K catalyst loaded became 100 g per liter. Then, the resulting honeycomb was fired in an electric furnace at 600°C for 1 hour to obtain an NOx adsorption
20 catalyst 26.

(Example 27)

[0059] First, the same cordierite honeycomb carrier as used in Example 1 was immersed in an aqueous H₃PO₄ solution. Since the carrier was porous, the aqueous H₃PO₄ solution infil-
25 trated into the interior of each cell wall. The excessive solution in the cells was removed by blowing, after which the carrier was dried. The amount of H₃PO₄ loaded was adjusted so that the moles of P element per unit volume of honeycomb

carrier became 1.24 times the moles of the K element contained in the K catalyst later wash-coated and loaded. When one time of immersion and drying failed to give a desired H_3PO_4 amount, the step of immersion and drying was repeated until the amount was reached. The honeycomb after drying was fired in an electric furnace at 700°C for 1 hour. On this honeycomb after firing was wash-coated the same slurry as obtained in Example 6, and the coated honeycomb was dried. This wash-coating and drying step was repeated if necessary until the amount of K catalyst loaded became 100 g per liter. The resulting honeycomb was fired in an electric furnace at 600°C for 1 hour, whereby an NO_x adsorption catalyst 27 was obtained.

(Example 28)

15 [0060] First, the same cordierite honeycomb carrier as used in Example 1 was immersed in an aqueous H_3PO_4 solution. Since the carrier was porous, the aqueous H_3PO_4 solution infiltrated into the interior of each cell wall. The excessive solution in the cells was removed by blowing, after which the carrier was dried. The amount of H_3PO_4 loaded was adjusted so that the moles of P element per unit volume of honeycomb carrier became 1.24 times the moles of the K element contained in the K catalyst later wash-coated and loaded. When one time of immersion and drying failed to give a desired H_3PO_4 amount, the step of immersion and drying was repeated until the amount was reached. The honeycomb after drying was fired in an electric furnace at 700°C for 1 hour. On the honeycomb after firing was wash-coated a slurry

obtained by mixing a zeolite and a silica sol, and the coated honeycomb was dried. The amount of SiO_2 loaded was adjusted so that the moles of Si element per unit volume of honeycomb carrier became 1.46 times the moles of the K element

5 contained in the K catalyst later wash-coated and loaded.

When one time of wash-coating and drying failed to give a desired SiO_2 amount, the step of wash-coating and drying was repeated until the amount was reached. The honeycomb after drying was fired in an electric furnace at 700°C for 1 hour.

10 On this honeycomb after firing was wash-coated the above-mentioned K catalyst slurry, and the coated honeycomb was dried. This wash-coating and drying step was repeated if necessary until the amount of K catalyst loaded became 100 g per liter. The resulting honeycomb was fired in an electric
15 furnace at 600°C for 1 hour, whereby an NO_x adsorption catalyst 28 was obtained.

(Example 29)

~~[0061]~~ An NO_x adsorption catalyst 29 was obtained in the same manner as in Example 27 except that the amount of H_3PO_4

20 loaded was adjusted so that the moles of P element per unit volume of honeycomb carrier became 0.14 time the moles of the K element contained in the K catalyst later wash-coated and loaded.

(Example 30)

25 ~~[0062]~~ An NO_x adsorption catalyst 30 was obtained in the same manner as in Example 28 except that the amount of H_3PO_4 loaded was adjusted so that the moles of P element per unit volume of honeycomb carrier became 0.14 time the moles of the

K element contained in the K catalyst later wash-coated and loaded.

(Example 31)

5 ~~[0063]~~ An NOx adsorption catalyst 31 was obtained in the same manner as in Example 1 except that the amount of H_3PO_4 loaded was adjusted so that the moles of P element per unit volume of honeycomb carrier became 0.0028 time the moles of the K element contained in the K catalyst later wash-coated and loaded.

10 (Example 32)

~~[0064]~~ An NOx adsorption catalyst 32 was obtained in the same manner as in Example 17 except that the amount of silica sol loaded was adjusted so that the moles of Si element per unit volume of honeycomb carrier became 0.0033 time the moles
15 of the K element contained in the K catalyst later wash-coated and loaded.

(Comparative Example 1)

~~[0065]~~ The above-mentioned K catalyst slurry was wash-coated on the same cordierite honeycomb carrier as used in
20 Example 1, and the coated carrier was dried. This coating and drying step was repeated if necessary until the amount of K catalyst loaded became 100 g per liter. The resulting honeycomb was fired in an electric furnace at 600°C for 1 hour to obtain an NOx adsorption catalyst 33.

25 (Comparative Example 2)

~~[0066]~~ The above-mentioned Na catalyst slurry was wash-coated on the same cordierite honeycomb carrier as used in Example 1, and the coated carrier was dried. This coating

and drying step was repeated if necessary until the amount of Na catalyst loaded became 100 g per liter. The resulting honeycomb was fired in an electric furnace at 600°C for 1 hour to obtain an NOx adsorption catalyst 34.

5 (Comparative Example 3)

10 ~~[0067]~~ The above-mentioned Li catalyst slurry was wash-coated on the same cordierite honeycomb carrier as used in Example 1, and the coated carrier was dried. This coating and drying step was repeated if necessary until the amount of Li catalyst loaded became 100 g per liter. The resulting honeycomb was fired in an electric furnace at 600°C for 1 hour to obtain an NOx adsorption catalyst 35.

(Comparative Example 4)

15 ~~[0068]~~ The above-mentioned K catalyst slurry was wash-coated on the same cordierite honeycomb carrier as used in Example 11, and the coated carrier was dried. This coating and drying step was repeated if necessary until the amount of K catalyst loaded became 100 g per liter. The resulting honeycomb was fired in an electric furnace at 600°C for 1
20 hour to obtain an NOx adsorption catalyst 36.

[Accelerated durability test]

25 ~~[0069]~~ The NOx adsorption catalysts 1 to 36 obtained in Examples 1 to 32 and Comparative Examples 1 to 4 were placed in an electric furnace and subjected to an accelerated durability test under the conditions of a temperature of 850°C, a period of 30 hours and a moisture content of 10% in furnace. For reference, a cordierite honeycomb carrier per se was also subjected to the same accelerated durability test.

[Suppressability of carrier deterioration]

~~[0070]~~ The NO_x adsorption catalysts 1 to 36 after the above test were observed for microstructure using an electron microscope, to examine the extent of generation of cracks.

- 5 Further, the catalysts using a cordierite honeycomb carrier were examined for flexural strengths before and after the test; and the catalysts using a metal honeycomb carrier were examined for tensile strengths of foil plate before and after the test. The results are shown in Tables 1 and 2.

Table 1

	Kind of honeycomb carrier	Kind of NOx adsorption catalyst component	Kind of anchor substance	Site of anchor substance
NOx adsorption catalyst 1	Cordierite	K	P	Mainly inside cell wall
NOx adsorption catalyst 2	Cordierite	K	Ti	Mainly inside cell wall
NOx adsorption catalyst 3	Cordierite	K	Ti	Mainly between cell wall and catalyst layer
NOx adsorption catalyst 4	Cordierite	Na	Ti	Mainly between cell wall and catalyst layer
NOx adsorption catalyst 5	Cordierite	Li	Ti	Mainly between cell wall and catalyst layer
NOx adsorption catalyst 6	Cordierite	K	Ti	Mainly in catalyst layer
NOx adsorption catalyst 7	Cordierite	K	Ti	Mainly in catalyst layer
NOx adsorption catalyst 8	Cordierite	K	Ti	Mainly in catalyst layer
NOx adsorption catalyst 9	Cordierite	K	Ti	Mainly in catalyst layer
NOx adsorption catalyst 10	Cordierite	K	Cr	Mainly inside cell wall
NOx adsorption catalyst 11	Metal	K	Ti	Mainly between cell wall and catalyst layer
NOx adsorption catalyst 12	Cordierite	K	P	Mainly inside cell wall
NOx adsorption catalyst 13	Cordierite	K	P	Mainly inside cell wall
NOx adsorption catalyst 14	Cordierite	K	P	Mainly inside cell wall
NOx adsorption catalyst 15	Cordierite	K	P	Mainly inside cell wall
NOx adsorption catalyst 16	Cordierite	K	P	Mainly inside cell wall
NOx adsorption catalyst 17	Cordierite	K	Si	Mainly inside cell wall
NOx adsorption catalyst 18	Cordierite	K	Si	Mainly inside cell wall
NOx adsorption catalyst 19	Cordierite	K	Si	Mainly inside cell wall
NOx adsorption catalyst 20	Cordierite	K	Si	Mainly inside cell wall

[0071]

Table 1-continued

	Amount of anchor substance added		Generation of cracks	Decrease in strength*2
	Weight of oxide per honeycomb unit volume*1	Molar ratio of anchor element to K, Na or Li		
NOx adsorption catalyst 1	24.1 g/l	0.67 time	None	16%
NOx adsorption catalyst 2	4.07 g/l	0.1 time	A little	37%
NOx adsorption catalyst 3	40.7 g/l	1 time	Slight	24%
NOx adsorption catalyst 4	40.7 g/l	1 time	Slight	30%
NOx adsorption catalyst 5	40.7 g/l	1 time	Slight	31%
NOx adsorption catalyst 6	40.7 g/l	1 time	Slight	32%
NOx adsorption catalyst 7	40.7 g/l	1 time	Slight	28%
NOx adsorption catalyst 8	40.7 g/l	1 time	Slight	30%
NOx adsorption catalyst 9	4.07 g/l	0.1 time	A little	35%
NOx adsorption catalyst 10	3.88 g/l	0.1 time	A little	38%
NOx adsorption catalyst 11	40.7 g/l	1 time	Slight	16%
NOx adsorption catalyst 12	80.0 g/l	2.21 times	None	11%
NOx adsorption catalyst 13	55.0 g/l	1.52 times	None	9%
NOx adsorption catalyst 14	45.0 g/l	1.24 times	None	8%
NOx adsorption catalyst 15	5.00 g/l	0.14 time	None	23%
NOx adsorption catalyst 16	1.00 g/l	0.028 time	None	40%
NOx adsorption catalyst 17	80.0 g/l	2.61 times	None	9%
NOx adsorption catalyst 18	55.0 g/l	1.79 times	None	10%
NOx adsorption catalyst 19	45.0 g/l	1.46 times	None	11%
NOx adsorption catalyst 20	24.1 g/l	0.79 time	None	20%

- 5

[illegible]

[0072]

Table 2.

	Kind of honeycomb carrier	Kind of NOx adsorption catalyst component	Kind of anchor substance	Site of anchor substance
NOx adsorption catalyst 21	Cordierite	K	Si	Mainly inside cell wall
NOx adsorption catalyst 22	Cordierite	K	Si	Mainly inside cell wall
NOx adsorption catalyst 23	Cordierite	K	Ti	Mainly inside cell wall
NOx adsorption catalyst 24	Cordierite	K	Cr	Mainly inside cell wall
NOx adsorption catalyst 25	Cordierite	K	P	Mainly in catalyst layer
NOx adsorption catalyst 26	Cordierite	K	Si	Mainly in catalyst layer
NOx adsorption catalyst 27	Cordierite	K	P	Mainly inside cell wall
			Ti	Mainly in catalyst layer
NOx adsorption catalyst 28	Cordierite	K	P	Mainly inside cell wall
			Si	Mainly between cell wall and catalyst layer
NOx adsorption catalyst 29	Cordierite	K	P	Mainly inside cell wall
			Ti	Mainly in catalyst layer
NOx adsorption catalyst 30	Cordierite	K	P	Mainly inside cell wall
			Si	Mainly between cell wall and catalyst layer
NOx adsorption catalyst 31	Cordierite	K	P	Mainly inside cell wall
NOx adsorption catalyst 32	Cordierite	K	Si	Mainly inside cell wall
NOx adsorption catalyst 33 (comparison)	Cordierite	K	-	-
NOx adsorption catalyst 34 (comparison)	Cordierite	Na	-	-
NOx adsorption catalyst 35 (comparison)	Cordierite	Li	-	-
NOx adsorption catalyst 36 (comparison)	Metal	K	-	-
Carrier only (reference)	Cordierite	-	-	-

Table 2-continued

	Amount of anchor substance added		Generation of cracks	Decrease in strength*2
	Weight of oxide per honeycomb unit volume*1	Molar ratio of anchor element to K, Na or Li		
NOx adsorption catalyst 21	5.00 g/l	0.16 time	Slight	29%
NOx adsorption catalyst 22	1.00 g/l	0.033 time	A little	46%
NOx adsorption catalyst 23	40.7 g/l	1 time	Slight	20%
NOx adsorption catalyst 24	38.8 g/l	1 time	Slight	18%
NOx adsorption catalyst 25	45.0 g/l	1.24 times	Slight	15%
NOx adsorption catalyst 26	45.0 g/l	1.46 times	Slight	19%
NOx adsorption catalyst 27	45.0 g/l	1.24 times	None	4%
	40.7 g/l	1 time		
NOx adsorption catalyst 28	45.0 g/l	1.24 times	None	5%
	45.0 g/l	1.46 times		
NOx adsorption catalyst 29	5.00 g/l	0.14 time	None	14%
	40.7 g/l	1 time		
NOx adsorption catalyst 30	5.00 g/l	0.14 time	None	8%
	45.0 g/l	1.46 times		
NOx adsorption catalyst 31	0.100 g/l	0.0028 time	Much	53%
NOx adsorption catalyst 32	0.100 g/l	0.0033 time	Much	59%
NOx adsorption catalyst 33 (comparison)	0 g/l	-	Very much	75%
NOx adsorption catalyst 34 (comparison)	0 g/l	-	Very much	79%
NOx adsorption catalyst 35 (comparison)	0 g/l	-	Very much	80%
NOx adsorption catalyst 36 (comparison)	0 g/l	-	Much	58%
Carrier only (reference)	0 g/l	-	None	2%

Notes for Table 2

- *1: Calculated from the difference in weights after and before firing. Therefore, presumed to basically be the weight of oxide of anchor substance. Some anchor substances have a form of a plurality of oxides, but each anchor substance is presumed to be represented by P_2O_5 , SiO_2 , TiO_2 or Cr_2O_3 .
- 5
- *2: Decrease (%) in strength after durability test relative to initial strength

~~[0073]~~ As shown in Table 1 and Table 2, each of the NOx adsorption catalysts 1 to 32 based on the present invention, as compared with the comparative NOx adsorption catalysts 33 to 36 containing no anchor substance, was little in crack
5 generation in carrier and low in strength decrease.

~~[0074]~~ As described above, the catalyst body of the present invention contains a substance which reacts with the alkali metal and/or alkaline earth metal used as a catalyst
10 component, in precedence over its reaction with the main component of the carrier used; therefore, even when the catalyst is subjected to a high temperature, the substance reacts with the alkali metal and/or alkaline earth metal and its reaction with the carrier is suppressed. As a result,
15 with the present catalyst, the deterioration of the carrier by the alkali metal and/or alkaline earth metal is suppressed, and the catalyst can be used over a long period.